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Research Paper

Microwave-assisted etherification of glycerol with *tert*-butyl alcohol over amorphous organosilica-aluminum phosphates

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ABSTRACT

The synthesis of organosilica-aluminum phosphates by a simple and cheap sol-gel method was carried out with varying amounts of two different silica precursors, 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (C) and (3-mercaptopropyl)trimethoxysilane (MPTMS); and several Al/P molar ratios. The solids were calcined in air, at different temperatures. The etherification of glycerol with *tert*-butyl alcohol was carried out in the liquid-phase under microwave irradiation and also by conventional heating. The incorporation of organosilica in the final solids took place in a 50–60%, as verified by TGA, ICP-MS, XPS and ^1H - ^{29}Si CP MAS NMR. The highest yield to h-GTBE (21%) was obtained at autogenous pressure, 85 °C and 15 min of reaction time under microwave, on the solid prepared with 10 mmol of C; Al/P = 1.5 and calcined at 250 °C. This material, with a balanced percentage of mesopores and macropores, also exhibited the highest number of acid sites determined by acid-base titration, as well as by results from TGA and by elemental analysis. The acidity and the hydrophilic character of the solids have been found to be key parameters for the catalytic activity, whereas porosity seems to be advantageous for the reusability of the solids, avoiding deactivation.

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1. Introduction

Over the last two decades, biodiesel has emerged as a competitive alternative to the fossil fuel due to intrinsic advantages such as low toxicity, biodegradability, renewability and biocompatibility. However, the formation of biodiesel generates glycerol as by-product (10 wt.% of the total biodiesel product). The growing trend in the biodiesel production has led to a large surplus of this glycerol and as a consequence a drop in its market value [1]. As the conventional application of glycerol could not cope with the excess production, several processes which employ glycerol to obtain added-value products are being investigated, including hydrogenolysis, dehydration, acetalisation, esterification, etherification and so on [2–5]. Among these different processes, etherification of glycerol to obtain glycerol *tert*-butyl ethers is an interesting alternative. In fact, di-*tert*-butyl glycerol ethers (DTBGs)

and tri-*tert*-butyl glycerol ether (TTBG), the so-called high ethers (h-GTBE), can be employed as excellent diesel and biodiesel additives due to their compatible physicochemical properties such as viscosity, flash point, cetane number, etc., providing a decrease in the emission of particulate matter, carbon oxide and carbonyl compounds in exhaust gases [6]. Furthermore, the low solubility of the mono-*tert*-butyl glycerol ethers (MTBGs) makes their use as fuel additives impossible. Therefore, the reaction must be shifted towards the formation of poly-substituted glycerol ethers.

Generally, the etherification of glycerol (G) is accomplished using isobutylene (IB) or *tert*-butyl alcohol (TBA) as reactants in the presence of acid catalysts. In particular, etherification of G with IB leads to higher yield values to h-GTBE than those obtained with TBA [7,8]. In fact, several papers have been published describing the production of poly-substituted ethers from G over different solid acid catalysts in the presence of IB [9–13]. However, the use of *tert*-butyl alcohol, a byproduct of polypropylene production, benefits mass transfer, suppresses isobutylene oligomerization and avoids using organic solvents in reaction mixtures.

Usually, the best catalytic results in the etherification of G with TBA have been obtained over acid resin catalysts, mainly over Amberlyst 15 (A-15) [7,14,15]. However, this A-15 usually presents

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a lack of thermal stability and suffers from swelling and shrinking in organic media. Furthermore, the sulfonic groups are the only part of the structure with hydrophilic character. For this reason, the water generated during the reaction would be adsorbed on these sulfonic groups, leading to a faster deactivation [16]. Thus, the synthesis of new catalytic systems remains challenging.

Frusteri et al. separately supported tungstophosphoric heteropolyacid (HPW-17) and a Nafion ionomer (N-17) on amorphous silica [16] attaining the best value of glycerol conversion (54%) on a phosphotungstic acid exchanged with cesium and supported on silica. Recently, cesium exchanged tungstophosphoric acid supported on tin oxide and different nanostructured MFI-type zeolites, have also been reported as good catalysts for this reaction [17,18]. González et al. [19] modified the surface and acid characteristics of three commercial Na-zeolites (mordenite, beta and ZSM-5) by different techniques. The best results were obtained on fluorinated beta zeolite ($Y_{h\text{-GTBE}} = 26\%$). They explained the differences in activity by the number of Bronsted acid sites and their strength, together with the accessibility of the reactants to these acid sites. In addition, sulfonated black carbons have exhibited a good catalytic performance in this reaction [20–22]. In fact, Gonçalves et al. [23] performed the reaction over different non-porous sulfonated black carbon catalysts obtained from biodiesel wastes, attaining a yield of 20% to h-GTBE with 80% of glycerol conversion at 120 °C and 8 h of reaction time. The “apparent” surface areas of those materials were lower than 10 m²/g. Thus, the population of sulfonic groups on the carbon surface seems to be essential for the etherification reaction.

Furthermore, we have recently reported this reaction on different sulfonic acid functionalized hybrid silicas obtained by oxidative cleavage of tetrasulfide bridges [24], concluding that a high density of acid sites, together with the non-porous structure, would explain the highest catalytic performance obtained ($Y_{h\text{-GTBE}}$ around 28%) at 75 °C and 24 h of reaction time over the S₅₀Ts₅₀O solid, synthesized by co-condensation of bis{3-(triethoxysilyl)propyl}tetrasulfide (BTEPTS) and tetraethyl orthosilicate (TEOS) with a molar ratio of 50-50 and subsequent oxidation of the tetrasulfide bridges with hydrogen peroxide. In addition, the hydrophilic character of the solids also played an important role in the deactivation of the catalysts.

On the other hand, we have also reported the excellent catalytic behavior of both pure and amorphous mesoporous aluminum phosphate (AlPO₄) and those modified by transition metals producing acrolein from pure glycerol in liquid phase [25] or aqueous solution of glycerol in gas phase [26]. The high water tolerance and the pore size exhibited by AlPO₄ are some advantageous properties for the etherification reaction, although the strength of its acid sites is not sufficient. In order to overcome this, we have synthesized aluminum phosphates in the presence of two different organosilicas, either containing a sulfonic group 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane or a sulfonic group precursor (3-mercaptopropyl)trimethoxysilane, by a sol-gel method similar to that employed in the synthesis of pure AlPO₄ [25]. The composition and the textural and physicochemical properties of the synthesized solids were also evaluated. Thus, the acidity of the solids was measured by acid-base titration and compared with the results obtained from thermogravimetric analysis (TGA) and from elemental analysis (sulfur content). The catalysts were tested in the etherification of glycerol with *tert*-butyl alcohol in the liquid phase by microwave irradiation and in some cases, with conventional heating for comparative purposes. The stability of the best catalysts was also tested by reusing them in subsequent reactions. Furthermore, a commercial Amberlyst-15 was also studied as a reference catalyst.

2. Experimental

2.1. Preparation of catalysts

The organosilica-aluminum phosphates were synthesized by a sol-gel method as follows: an aqueous solution of AlCl₃·6H₂O was kept under magnetic stirring (900 rpm) and mixed with H₃PO₄ (85 wt.%) in an ice-water bath. After 1 h, 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (C) or (3-mercaptopropyl)trimethoxysilane (MPTMS) was added dropwise. Then, aqueous ammonia was slowly added until a pH of 5 was reached. The final synthesis gel was then kept at room temperature for 24 h. The solid obtained was filtered off and washed with isopropyl alcohol and dried at 120 °C for 24 h. Finally, the solids were calcined. The catalysts obtained using C as organosilica will be denoted as C(x)AlPO(y)-T where x is the mmol of organosilica added to the initial mixture, ranging from 2.5 to 10; y is the Al/P molar ratio (1.5, 1 or 0.5) and T is the calcination temperature (250 or 310 °C). In the material prepared with the other organosilica precursor, 10 mmol of MPTMS was added to the initial mixture, the Al/P molar ratio was 1 and the calcination temperature was 210 °C. This solid will be denoted as MPTMS(10)AlPO(1). After calcination, this solid was treated with H₂O₂ in order to oxidized the thiol group (–SH) to sulfonic group (–SO₃H) in accordance with a previously reported procedure [27]. In this case, the oxidation post-treatment was carried out during 3 h at room temperature and also at 50 °C using conventional heating and microwave (*Milestone Flexiwave Microwave*) for comparison purposes. These materials will be denoted as MPTMS(10)AlPO(1)-(T) where T is the oxidation temperature. The solid oxidized at room temperature will be denoted as MPTMS(10)AlPO(1)-RT and those oxidized using microwave heating will be denoted with Mw at the end of the name. Finally, all the solids were powder screened to <0.149 mm, to avoid internal diffusion limitations in the reactions.

2.2. Characterization of the catalysts

XRD powder diffraction patterns were obtained using a Discover (Bruker) diffractometer equipped with Cu K α radiation. Finely ground samples were scanned at a speed of 2 °/min (2 θ = 2–70°). Textural properties were determined from the N₂ adsorption-desorption isotherms at –196 °C, using a Micromeritics ASAP 2010 apparatus. Prior to measurements, all the samples were degassed at 120 °C for 12 h. The specific surface area of each solid, S_{BET}, was determined by using the BET method at relative pressures in the range p/p₀ = 0.05–0.3 assuming a cross-sectional area of 0.162 nm² for the nitrogen molecule. The values of pore volume and the pore size distributions were calculated by the Barret-Joyner-Halenda (BJH) method. The C, H, N and S content was determined by elemental analysis, according to the Dumas method, based on the complete combustion of the sample in an oxygen-enriched atmosphere and the subsequent analysis of the gases by gas chromatography with a TCD detector. A Eurovector Elemental Analyser EA3000 equipped with Callidus software (EuroVector SpA, Milan, Italy) was used. Regarding the aluminum, phosphorus and silicon content in the materials, an Inductive Coupled Plasma (ICP) in a Philips PU 70,000 sequential spectrometer equipped with an Echelle monochromators (0.0075 nm resolution) and coupled to Mass Spectrometry was used. XPS spectra were recorded with a SPECS Phobos HAS 3500 150 MCD, being the residual pressure in the analysis chamber 5×10^{-9} Pa. Accurate binding energies were determined with respect to the position of the Si 2p peak at 103.4 eV. The peaks were decomposed using a least-squares fitting routine (Casa XPS software) with a Gaussian-Lorentzian (70:30) using Shirley baselines. Thermogravimetric analyses (TGA) were recorded on a Setaram Setsys 12 thermal analysis station by heating in air from 30 to

600 °C at a rate of 10 °C min⁻¹. ²⁷Al, ³¹P MAS NMR spectra and ¹H–²⁹Si cross-polarization (CP) MAS NMR spectra were recorded on a BRUKER AVANCE 400WB spectrometer using a 4 mm BRUKER double resonance MAS probe.

The acidity was determined using the following procedure. Aliquots of 50 mg of the material were stirred with 20 g of a 2 M NaCl solution at room temperature for 24 h. Then, the solid was filtered off and the resulting solution titrated with a 0.025 M NaOH solution using phenolphthalein as indicator.

2.3. Catalytic reaction

Microwave experiments were carried out in a CEM-DISCOVER apparatus with PC control. Experiments were performed on a closed vessel (pressure controlled) under continuous stirring. The microwave method was generally power-controlled, where the reaction mixture was irradiated until the temperature selected, measured by an infra-red probe, was reached (Fig. S1).

In a typical run, the composition of the reaction mixture was: 0.4 g of glycerol, TBA/G molar ratio of 4 and constant catalyst loading of 5 wt.% (referred to initial glycerol mass). The total volume of the reactant mixture was 2 mL. The reaction temperature was 85 °C and after 15 min of reaction, the sample was cooled down in an ice bath, filtered off and subsequently analyzed. Other experiments at different reaction times were performed under the same conditions.

For comparative purposes, the liquid-phase etherification reaction between G and TBA using conventional heating was carried out in a round-bottom flask (100 mL) with magnetic stirring at autogenous pressure. The reaction conditions were similar to those using Mw, except for the reaction time and temperature. At the end of the experiments, the reactor was cooled down in an ice bath before the sample was taken.

Furthermore, blank experiments using either microwave or conventional heating, showed that the mixture of TBA/G did not react in the absence of catalyst under the experimental conditions employed.

The identification of the products was carried out by GC-MS (VARIAN CP 3800, QUADRUPOLE MS 1200) equipped with a Supelcowax 10 capillary column, 100% ethylene glycol (30 m × 0.25 mm × 0.25 μm), according to the characterization data reported by Jamróz et al. [28]. The quantitative analysis was carried out by GC in a Hewlett Packard 5890 series II, also equipped with a Supelcowax 10 capillary column, and a FID detector, using 4-chlorotoluene as an internal standard [24]. The analysis program was: 60 °C for 6 min heating at 20 °C/min until 240 °C with an analysis time of 25 min. The conversion of glycerol (X_G) and product selectivity (S) were determined by the following equation:

$$X_G(\%) = \frac{\text{mmol of produced TBGs}}{\text{starting mmol of G}} \times 100$$

$$S_i(\%) = \frac{\text{mmol of compound i}}{\text{mmol of produced TBGs}} \times 100$$

Site Time Yield (STY) was calculated as mmol of produced h-GTBE per mmol of active specie SO₃H (calculated from TGA) per hour. It should be noted that secondary reactions coming from glycerol were never obtained under the experimental conditions employed. Furthermore, in order to check the reliability of the quantification procedure, at the end of some experiments, the DTBGs and TTBG products, which were not commercially available, were isolated from the final product by column chromatography (1:9 ethyl acetate/hexane). The results obtained (X_G and Si) were slightly lower (<10%) than those obtained by chromatography analysis.

At the end of the reaction, the catalyst was recovered, washed with ethanol and dried at 80 °C. Afterwards, it was tested again following the same procedure as described above. To study the reusability of the solids, several reactions under the same conditions with the same amount of catalyst were carried out, in order to have enough catalyst to test it again in subsequent runs.

3. Results and discussion

3.1. Characterization of catalysts

Regarding to textural properties, all the C(x)AlPO(1.5)-T exhibited isotherms type IV with a step at a relative pressure around 0.6–0.9 (Fig. 1). This is typical of pores in the high mesopore range. In fact, the solids showed a wide pore size distribution with a maximum ranging from 13 nm for C(2.5)AlPO(1.5)-250, C(4)AlPO(1.5)-250 and C(4)AlPO(1.5)-310 materials to 19 nm for C(10)AlPO(1.5)-250. Furthermore, as can be seen in Table 1, the S_{BET} did not change as the amount of organosilica (C) increased from 2.5 to 4 mmol in the initial mixture, whereas the S_{BET} decreased when the amount of C was 10 mmol, favoring the formation of macropores in the final material. On the other hand, the solids with an Al/P molar ratio ≤ 1, e.g., C(10)AlPO(1)-250, MPTMS(10)AlPO(1) and C(10)AlPO(0.5)-250 exhibited mainly type II isotherms, characteristic of macroporous materials, as confirmed by the pore size distribution (Fig. 2), although some mesoporosity was also observed. The decrease in the surface area, as well as the change in the mesoporosity, could be related to a lower amount of Al in the initial mixture. In fact, the material with the lowest Al/P ratio (0.5) exhibited the lowest surface area value (9 m²/g) and the highest percentage of macropores (78%), Table 1. Furthermore, the oxidation treatment did not induce significant changes in the textural properties of the MPTMS(10)AlPO(1), independently of both the oxidation temperature and the way of heating.

All the solids exhibited similar XRD patterns (Fig. S2), typical of metal phosphates and silica with amorphous character, suggesting that the sulfonation, calcination temperature or Al/P ratio did not induce any changes in the morphology of the solids studied.

The structure of the solids was characterized by ¹H–²⁹Si CP MAS NMR, ²⁷Al and ³¹P NMR spectroscopy for samples with different compositions. The ¹H–²⁹Si CP MAS NMR spectra of the solids are shown in Fig. 3. Distinct resonances can be clearly observed for the organosiloxane ($T^m = \text{RSi(OSi)}_m(\text{OH})_{3-m}$, m = 1–3 between –50 and –70 ppm) indicating the good incorporation of C in the final material. The deconvolution of the T^m signal showed that T^3 species were the most representative in the materials, Fig. 3 and Table 2. This could be ascribed to the fact that H₃PO₄ favors the condensation of the silica over the hydrolysis, as has been previously observed by Cihář et al. [29] in the hydrolysis and polycondensation of ethyl silicates. Furthermore, some unexpected signals associated to siloxane groups ($Q^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, n = 2–4 between –90 and –120 ppm), were also observed. These Q^n signals were generally lower than the T^m signals, and can be ascribed to the rupture of some C-Si bonds of C due to the acid media and/or the calcination temperature. In fact, the intensity of the Q^n signals increased either as the amount of H₃PO₄ increased, or as the calcination temperature increased from 250 to 310 °C, Fig. 3. However, the existence of a possible interaction between Si and Al from Si CP spectra is not reliable enough, since the chemical shift for Si-O-Al is in the same range as that for Si-OH [30].

The ²⁷Al MAS NMR spectra of the solids are shown in Fig. 4. All the solids exhibited three components, one of them around +34–42 ppm, which is a typical resonance of tetrahedral Al [31,32], and two additional resonances at around +10 ppm and –13 ppm, which can be assigned to Al species partially coordinated with

Table 1

Textural properties, sulfur content determined by different techniques, silicon content, Al/P molar ratio and acidity-related properties of all the solids studied.

Catalyst	Textural Properties				Composition and acidity					
	S _{BET} (m ² /g)	V _p (cm ³ /g)	Mesopores (%)	Macropores (%)	S _{measured} ^a (mmol S/g)	S _{oxidized} ^b (%)	Si ^c (mmol Si/g)	Al/P ^c molar ratio	Acidity ^d (mmol H ⁺ /g)	Acidity ^e (mmol SO ₃ H/g)
A-15 ^f	39	0.34	–	–	–	–	–	–	4.7	–
C(2.5)AlPO(1.5)-250	200	0.77	80	20	0.3	–	0.3	1.2	0.7	0.3
C(2.5)AlPO(1.5)-310	251	0.84	79	21	0.3	–	0.4	1.2	0.7	0.3
C(4)AlPO(1.5)-250	210	0.68	88	12	0.3	–	0.4	1.2	0.7	0.4
C(4)AlPO(1.5)-310	242	0.75	88	12	0.3	–	0.4	1.2	0.9	0.4
C(10)AlPO(1.5)-250	79	0.42	60	40	1.1	–	1	0.9	1.3	1.2
C(10)AlPO(1)-250	41	0.42	47	53	0.9	–	0.9	0.7	1.3	0.7
C(10)AlPO(1)-310	45	0.31	48	52	0.9	–	0.9	0.7	1.3	0.7
C(10)AlPO(0.5)-250	9	0.18	22	78	1.0	–	0.8	0.3	1.6	0.9
MPTMS(10)AlPO(1)	59	0.51	53	47	1.0	–	1.2	0.6	0.2	–
MPTMS(10)AlPO(1)-RT	60	0.60	52	48	1.0	29	1.2	0.6	0.7	–
MPTMS(10)AlPO(1)-50	51	0.44	50	50	1.0	83	1.2	0.6	1.1	–
MPTMS(10)AlPO(1)-50Mw	53	0.54	50	50	1.0	79	1.2	0.6	1.1	–

^a Determined by Elemental Analysis (Dumas method).

^b Determined by deconvolution of the XPS spectra (as percentage of the total S content).

^c Determined by ICP-MS.

^d H⁺ content determined by titration.

^e (mmol organic sulfonic group/g sample) calculated from TGA.

^f Characterization provided by the supplier.

Table 2

MAS NMR isotropic chemical shifts.

Catalyst	δ_i (ppm)		
	¹ H- ²⁹ Si CP	²⁷ Al	³¹ P
	T ^m		
C(4)AlPO(1.5)	-49.1(1) ^a ; -60.0(22); -66.4	-45.0(6); -12.2(58); 13.6(6); 42.6	-21.2(50); -13.8
C(4)AlPO(1.5)-250	-50.6(1); -60.5(28); -67.1	-11.5(22); 11.0(21); 36.5	-25.8(98); -11.5
C(4)AlPO(1.5)-310	-54.3(13); -61.5(60); -68.8	-11.1(40); 13.2(6); 40.3	-25.8(73); -14.9
C(10)AlPO(1.5)-250	-54.8(7); -61.4(23); -66.4	-13.7(15); 11.1(9); 38.4	-26.1(96); -13.8
C(10)AlPO(1)-250	-54.8(14); -67.9	-14.9(49); 7.2(10); 37.3	-27.5(53); -18.9(42); -9.8
C(10)AlPO(0.5)-250	-51.6(4); -62.0(35); -69.5	-16.4(63); 4.5(23); 34.6	-26.9(40); -20.0(45); -9.8(12); -1

^a Percentage.

hydroxyl groups in a penta- and octahedral coordination respectively [31]. As can be seen in Fig. 4, the calcination of the C(4)AlPO(1.5) at 250 °C caused a decrease in the peaks associated with coordinated penta- and octahedral Al species, due to the water removal as was expected. However, as the calcination temperature increased from 250 to 310 °C, an increase in the octahedral component was observed. This fact has been previously reported by Prabakar et al. [33] in some aluminosilicate gels. Thus, when silicon is present in the gel, the tetrahedral-octahedral conversion of Al sites may be preceded by the migration of protons onto the oxygen atoms surrounding Al atoms. This migration of protons onto the Al sites is probably due to the fact that the partial charge on the oxygen in $\text{AlO}_{4/2}^-$ is greater than in $\text{SiO}_{3/2}(\text{OH})$. This would explain the growth of the octahedral ²⁷Al resonance at the expense of the tetrahedral resonance, indicating an interaction between Si and Al in our materials. This interaction seems to be more evident as the Al content in the materials decreases. In fact, as the Al/P ratio decreases, the peak corresponding to tetrahedral Al diminishes, whereas the octahedral resonance rises significantly. Consequently, the interaction between phosphorous and aluminum was much lower as the Al/P ratio decreased.

For its part, the ³¹P MAS NMR spectra of the C(x)AlPO(1.5)-250 showed a broad signal at -26 ppm (Fig. 5 and Table 2), which suggests that the environments of phosphorous nuclei are mainly P(OAl)_4 , regardless of the amount of C. However, as the Al/P ratio decreased, the peak became broader and more asymmetric. In fact, the broadest signal was obtained for C(10)AlPO(0.5)-250. The asymmetric shape in the low-field values of this signal, as well as the emergence of a new signal at -1 ppm, suggests the existence of

P–O–P bonds. This fact agreed with the results obtained from ²⁷Al NMR for the C(10)AlPO(x)-250 solids, indicating that as the Al content decreases, the interaction between Al and Si increases, causing a less interaction between Al and P.

The amount of Si measured by ICP-MS, Table 1, did not change in the materials in which C increased from 2.5 to 4, although when C rose from 4 to 10, the Si in the material also increased. However, the incorporation of the organosilica in the materials was around 50–60% of the initial amount of the organosilica employed.

Thermogravimetric analyses (TGA) were performed to ascertain the thermal stability of the catalysts as well as to confirm and quantify the introduction of both, the thiol groups and the sulfonic acid groups. First of all, the TGA of the non-calcined samples were very similar with three weight losses up to 600 °C, as can be seen in Fig. S3A. The first weight loss, under 200 °C, can be attributed to the removal of physisorbed water and isopropyl alcohol (11.3%), while the second one, up to 310 °C, that is greater, can be ascribed to the removal of ammonium chloride (14%), as was previously reported for an aluminum-vanadium-phosphate system (AlVPO) synthesized at similar conditions [34]. The third weight loss, observed between 350 and 600 °C, has been related in the literature [9,13,35] to the loss of organosulfonic acid groups (C). The TGA profile (Fig. S3B) obtained for AlPO(1.5)-250, synthesized under the same conditions but without the addition of the organosilica precursor, allows us to confirm this assignation, given that no weight loss in this range was observed in the profile. As can be seen in Fig. 6, the greatest weight loss in this range (~20%) was obtained for C(10)AlPO(1.5)-250 material. Based on the TGA results, the solids were calcined at 250 °C for four hours. Furthermore, some of them

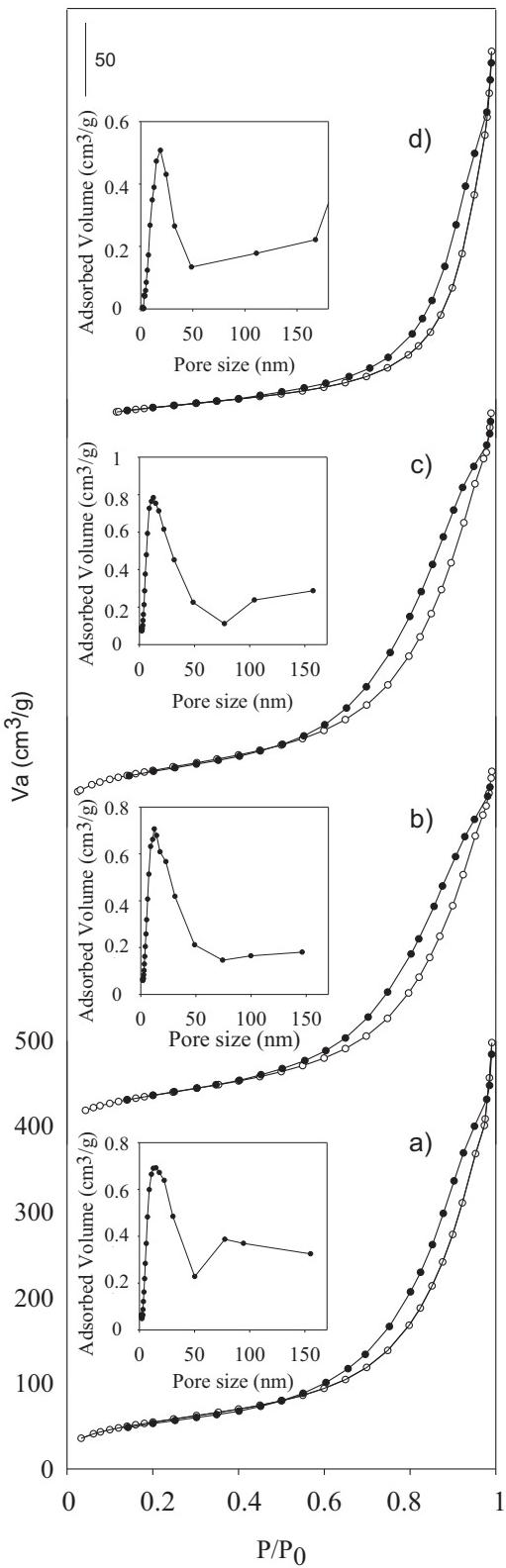


Fig. 1. Nitrogen adsorption-desorption isotherms of a) C(2.5)AlPO(1.5)-250, b) C(4)AlPO(1.5)-250, c) C(4)AlPO(1.5)-310 and d) C(10)AlPO(1.5)-250. Adsorption (\circ) and desorption (\bullet) branches.

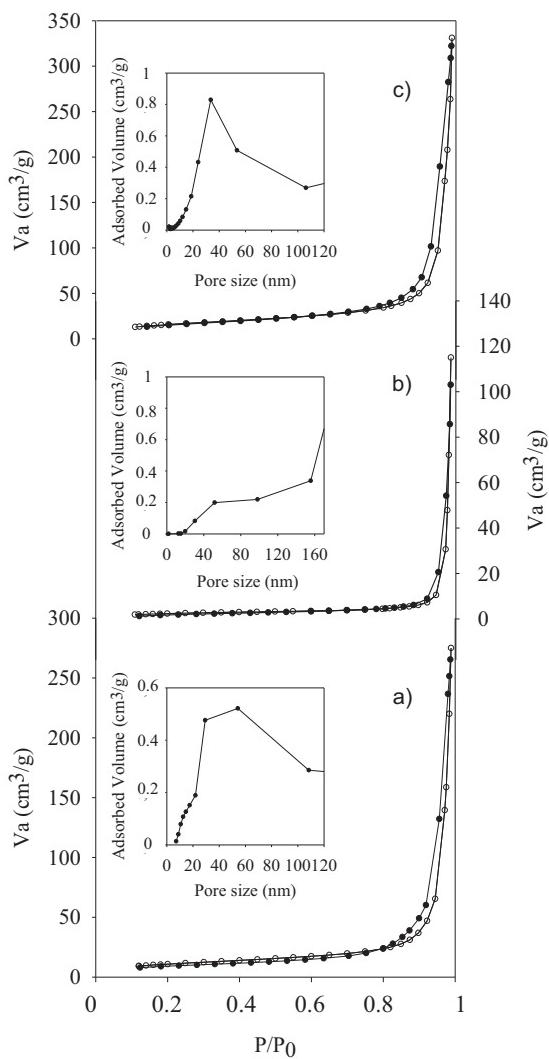


Fig. 2. Nitrogen adsorption-desorption isotherms of a) C(10)AlPO(1)-250, b) C(10)AlPO(0.5)-250 and c) MPTMS(10)AlPO(1). Adsorption (\circ) and desorption (\bullet) branches.

were calcined at 310 °C. Thus, the TG profiles of the solids calcined at 250 °C (Fig. 6) showed that the weight loss due to the removal of physisorbed water and isopropyl alcohol was less than 6% in any case, whereas the non-calcined samples lost around 10–15%. Moreover, the weight loss related to the ammonium chloride was less for the calcined solids than that observed for the non-calcined solids, as expected. In fact, for all the solids studied, the weight loss was less than 1.5% except for C(10)AlPO(0.5)-250, which lost 2.4%. Very similar weight losses were observed for the solids calcined at 310 °C in these ranges, Fig. S3B.

3.2. Determination of the solids acidity

The weight loss between 350 and 600 °C in the TG profiles allow us to obtain the amount of sulfonic group in accordance with Gonzalez et al. [13]. In Table 1 such values (mmol SO₃H/g), which were different to those values of acidity obtained by titration, are shown. This difference was greater for the C(10)AlPO(1)250 and C(10)AlPO(0.5)250 solids, which interestingly also presented the highest percentage of nitrogen (from NH₄⁺) among the calcined solids, Table S1. One possible explanation for this difference in the acidity values could be due to additional titration of such NH₄⁺ groups in the solids, resulting in an excess error in the acidity

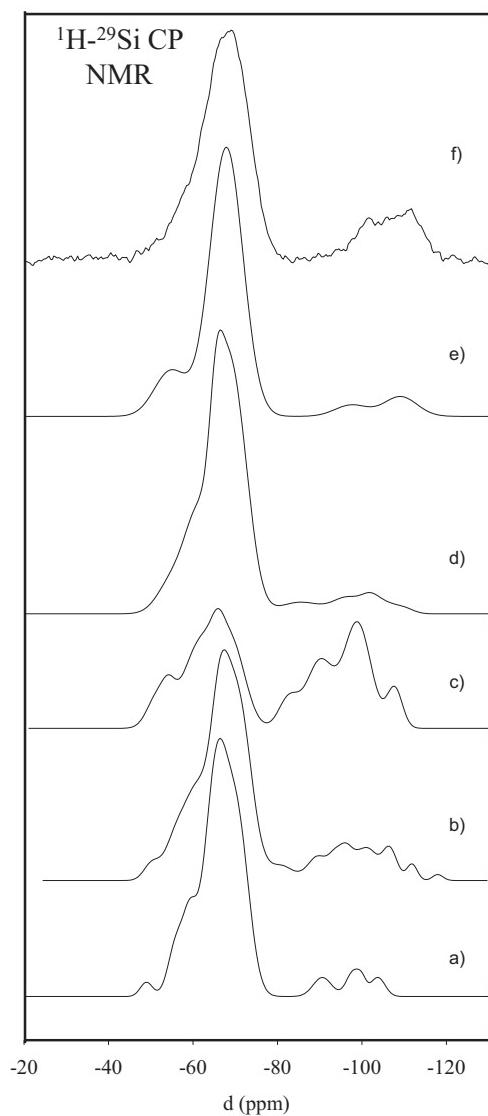


Fig. 3. ^{29}Si NMR spectra for: a) C(4)AlPO(1.5), b) C(4)AlPO(1.5)-250, c) C(4)AlPO(1.5)-310, d) C(10)AlPO(1.5)-250, e) C(10)AlPO(1)-250 and f) C(10)AlPO(0.5)-250.

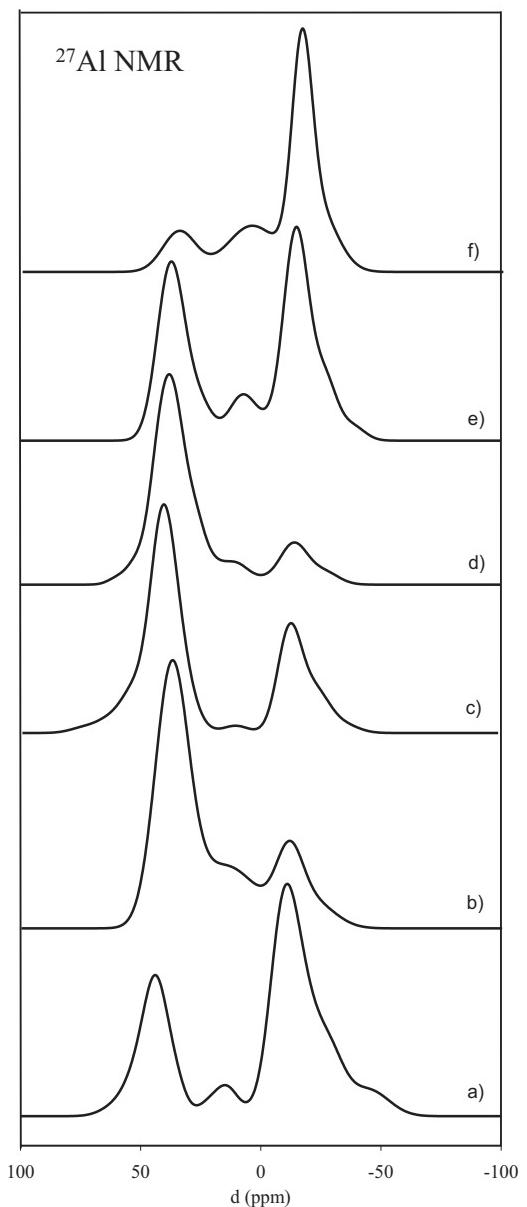


Fig. 4. ^{27}Al NMR spectra for: a) C(4)AlPO(1.5), b) C(4)AlPO(1.5)-250, c) C(4)AlPO(1.5)-310, d) C(10)AlPO(1.5)-250, e) C(10)AlPO(1)-250 and f) C(10)AlPO(0.5)-250.

measured by titration. Thus, it could be concluded that titration is not an accurate way to determine the acidity of these materials. Contrary to these results, a very good relation between the S content obtained by elemental analysis and the amount of S by TGA was found. Furthermore, given that all the sulfur in the samples C(x)AlPO(y) is in sulfonic form, both ways to determine the acidity could be adopted.

In the case of the oxidized MPTMS(10)AlPO(1) catalysts, the mmol of sulfonic acid groups were calculated from the amount of S obtained by elemental analysis and those obtained from XPS (S_{oxidized}). In fact, the peak around 169 eV is assigned to the sulfur in sulfonic form ($-\text{SO}_3\text{H}$) [13,35], whereas the peak around 164 is related to the sulfur in the thiol form ($-\text{SH}$). As can be seen in Table 1 and Fig. S4, when the oxidation was performed at 50 °C, regardless of the way of heating, the percentage of S_{oxidized} was higher than that obtained at room temperature. However, with conventional heating the percentage was slightly higher (83%) than when using microwave (79%). Hence, the temperature promoted the oxidation of thiol to sulfonic groups.

3.3. Catalytic reaction

Independently of the heating method used, the reaction products obtained were MTBGs, DTBGs and TTBG. Generally, a small amount of isobutylene (<7%) was obtained but it was not considered for quantification because it came from TBA, which was in excess. It should also be noted that secondary reactions coming from glycerol were never obtained under these conditions.

3.3.1. Microwave-assisted etherification of glycerol

Fig. 7 shows the evolution of the glycerol conversion and the selectivity to MTBGs and h-GTBE in function of reaction time for C(10)AlPO(1)-250 catalyst at two different reaction temperatures, 75 and 85 °C. As can be seen, an increase in the reaction temperature from 75 to 85 °C led to an increase, not only in the glycerol conversion, but also in the selectivity to h-GTBE, whereas the selectivity to MTBGs decreased. Furthermore, regardless of the reaction temperature, the glycerol conversion increased from 3 to 15 min of

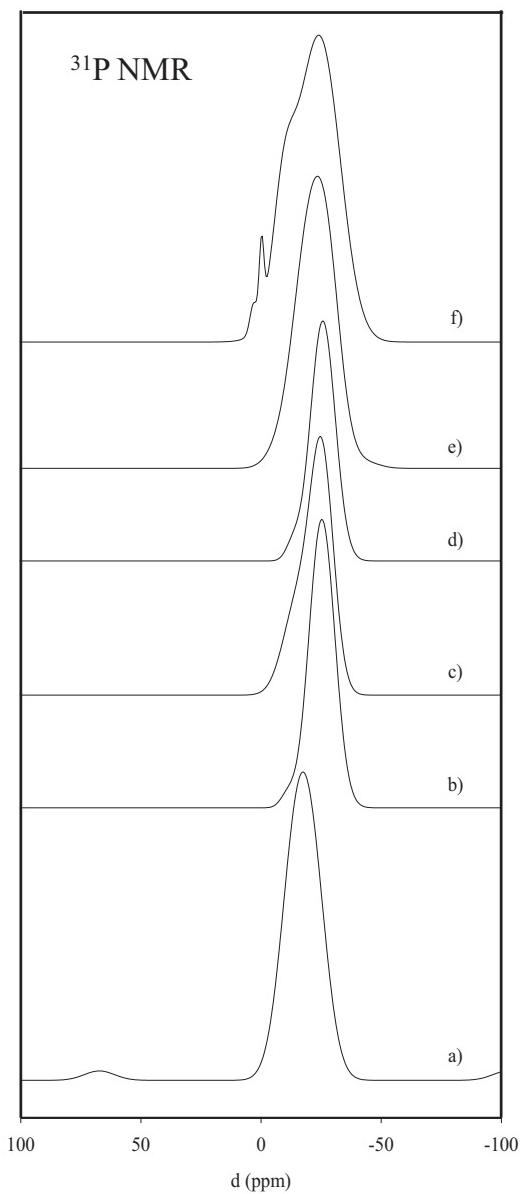


Fig. 5. ^{31}P NMR spectra for: a) C(4)AlPO(1.5), b) C(4)AlPO(1.5)-250, c) C(4)AlPO(1.5)-310, d) C(10)AlPO(1.5)-250, e) C(10)AlPO(1)-250 and f) C(10)AlPO(0.5)-250.

reaction, although the increase after 10 min was less pronounced than that obtained at shorter reaction times. After 15 min, the glycerol conversion remained practically constant. According to selectivity, the formation of MTBG decreased slightly in function of reaction time, whereas the formation of h-GTBE increased. Analogously to the glycerol conversion, the increase in the selectivity to h-GTBE was less pronounced after 10 min of reaction time and almost negligible after 15 min. Thus, it could be assumed that after 15 min, the equilibrium was almost reached. In this respect, based on the values of the equilibrium constants reported by Vlad et al. [36] and Kiatkittipong et al. [37], the theoretical conversion value in the equilibrium at 85 °C under our reaction conditions, should be 91% taking into account only the first step of the reaction, the formation of MTBGs.

Table 3 shows the catalytic behavior of all the solids studied in the etherification reaction of glycerol with *tert*-butyl alcohol after 15 min of reaction. The C(10)AlPO(1.5)-250 catalyst was the most active, exhibiting the highest values of conversion and yield to h-GTBE not only at 15 min of reaction, 83% and 21% respectively, but

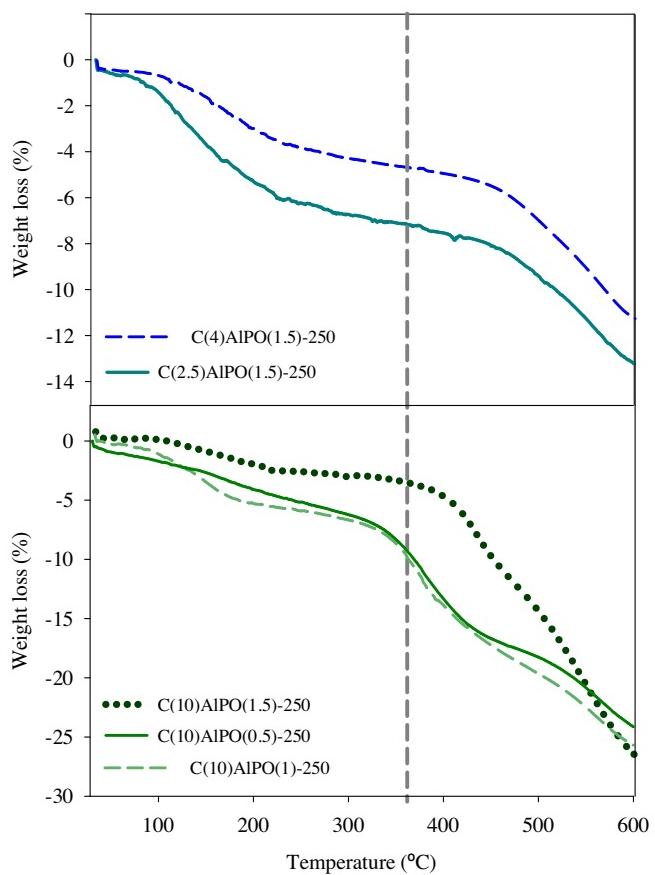


Fig. 6. TG analysis for the organosilica-aluminum phosphates.

also at 5 min, 56% and 13%, respectively. This catalyst also showed the highest acidity value (1.2 mmol $\text{SO}_3\text{H}/\text{g}$). In fact, as can be seen in Fig. S5, the acidity of the catalysts strongly influences conversion and yield to h-GTBE values, a linear relationship existing from data obtained at 15 min. Moreover, a similar ratio exists between the acidity values (0.58) and those of conversion (0.54 at 15 min and 0.53 at 5 min) for C(10)AlPO(1) and C(10)AlPO(1.5). It should be noted that there were no differences in the catalytic behavior of the C(2.5)AlPO(1.5)-250 and C(4)AlPO(1.5)-250, which exhibited similar acidity values and similar textural properties. An increase in the calcination temperature for these two solids led to a small increase in the values of conversion. This fact could be explained by the increase in the surface area that the solids calcined at 310 °C suffered, and hence, a better distribution of the acid sites. Moreover, the similar conversion values obtained over C(10)AlPO(1)-250 and C(10)AlPO(1)-310 (42 and 45%) would support the previous explanation given that their textural properties remained unchanged.

The present results confirm, as has been previously reported [16,24], that the reaction mechanism occur via a fast protonation of TBA on acid sites, giving rise to a tertiary carbocation that reacts with glycerol, generating the first MTBGs. Another TBA molecule reacts with MTBGs to form the DTBGs, which finally form the TTBG in a subsequent reaction with another TBA molecule. Logically, the TTBG formation would be less favoured with respect to that of DTBGs and especially of MTBGs, due to steric hindrance of the *t*-butyl groups bonded to glycerol. Moreover, some amount of IB coming from the dehydration of the alcohol, and water were formed as by-products. These by-products could compete with TBA and glycerol for the acid sites causing the equilibrium to be reached after 15 min of reaction. To ensure that water would promote the deactivation of the solids, an experiment consisting in the addition

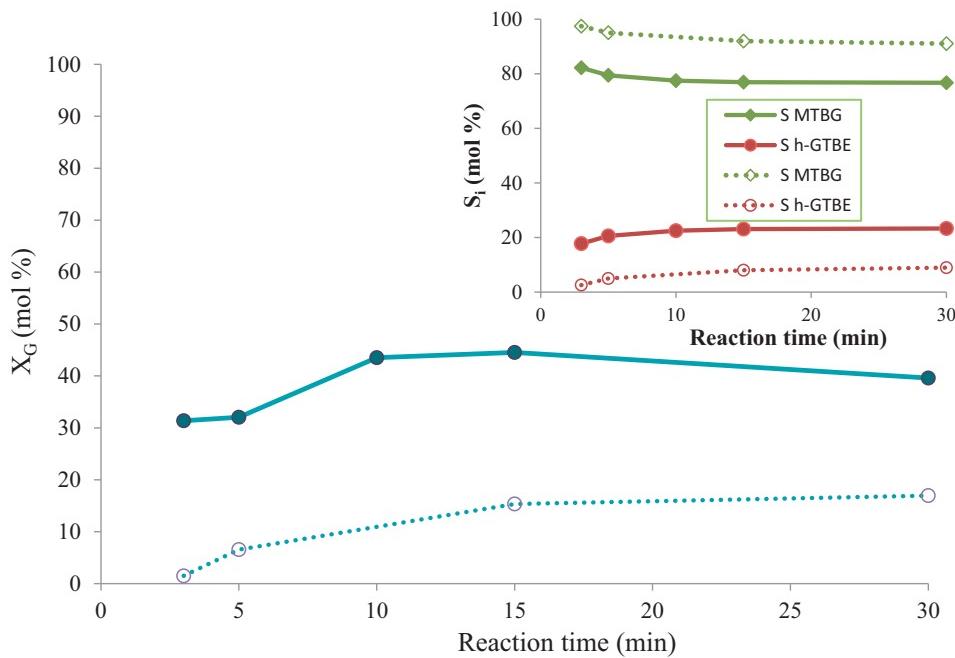


Fig. 7. Study of the variation of glycerol conversion and selectivity to the different products at two different temperatures, 75 °C (dashed lines) and 85 °C (solid lines), with time of reaction on C(10)AlPO(1)-250 under microwave irradiation. Reaction conditions: 5.0 wt.% of catalyst referred to the starting amount of glycerol, TBA/G molar ratio = 4.

Table 3

Catalytic behavior of the different catalysts after 15 min. Reaction conditions: 5.0 wt.% of catalyst referred to initial glycerol, TBA/G ratio = 4, reaction temperature 85 °C under microwave irradiation. Site Time Yield (STY) was calculated as mmol of produced h-GTBE per mmol of active species SO₃H (calculated from TGA) per hour.

Catalyst	Conversion (mol%)	S _{MTBG} (mol%)	S _{h-GTBE} (mol%)	Y _{h-GTBE} (mol%)	Site Time Yield (STY) (h ⁻¹)
A-15 ^a	45	87	13	6 (1) ^b	33
A-15	43	83	17	7 (1)	13
A-15 ^c	10	90	10	1	2
C(2.5)AlPO(1.5)-250	11	93	7	1	29
C(2.5)AlPO(1.5)-310	17	87	13	2	58
C(4)AlPO(1.5)-250	8	92	8	1	22
C(4)AlPO(1.5)-310	18	86	14	3	65
C(10)AlPO(1.5)-250 ^a	56	76	24	13 (1)	282
C(10)AlPO(1.5)-250	83	75	25	21 (1)	152
C(10)AlPO(1.5)-250 ^c	45	82	18	8 (1)	58
C(10)AlPO(1)-250	42	80	20	8 (1)	99
C(10)AlPO(1)-310 ^a	30	79	21	6 (1)	223
C(10)AlPO(1)-310	45	77	23	10 (1)	124
C(10)AlPO(0.5)-250	59	77	23	14 (1)	135
MPTMS(10)AlPO(1)-RT	6	93	7	<1	20
MPTMS(10)AlPO(1)-50	21	87	13	3	31
MPTMS(10)AlPO(1)-50Mw	14	90	10	1	11

^a Reaction time = 5 min.

^b In parenthesis, yield to glycerol triether (%).

^c Addition of 0.1 mL of water after 5 min of reaction. Total reaction time = 15 min.

of 0.1 mL of water after five minutes of reaction time, was carried out on C(10)AlPO(1.5) and then, the reaction continued for 10 more minutes. The results showed in Table 3 indicate a decrease of both conversion and selectivity to h-GTBE, whereas the selectivity to MTBGs increased slightly. Hence, the water formed in each step of the reaction promotes the deactivation of the catalysts, clearly coinciding with the results previously obtained with other catalytic systems [19,38,39]. This fact was even more evident when A-15 was employed as a catalyst. The conversion values changed from 45% to 10% and the yield to h-GTBE decreased from 6% to 1%, Table 3. Likewise, at isoconversion (42–45%) both C(10)AlPO(1) catalysts were more selective to h-GTBE than A-15, in spite of its higher number of acid sites. These results could be ascribed to the higher hydrophobic character of the Amberlyst, as aforementioned, since the sulfonic groups are the only hydrophilic part of its structure, so the water generated during the reaction would

be adsorbed on these sulfonic groups, leading to a faster deactivation. The organosilica-aluminum phosphates present a higher hydrophilic character due to the presence of Al-OH, P-OH and Si-OH groups and thus, the water generated in each step could be adsorbed on this hydrophilic part, mitigating the deactivation of the sulfonic acid sites and making this a very interesting material to be considered in using raw glycerol as a reactant.

Regarding the oxidized MPTMS(10)AlPO(1) catalysts, the glycerol conversion was higher for those in which the percentage of the oxidized thiol groups was superior, Table 1. This means that, as with C(x)AlPO(y)-250, the catalysts with higher amount of sulfonic groups, gave the highest conversion value. Comparing the conversion values attained on MPTMS(10)AlPO(1)-50 and C(10)AlPO(1)-250 (21 and 42%, respectively), it can be observed that the conversion was higher on C(10)AlPO(1)-250, although both solids exhibited very similar textural properties, as well as

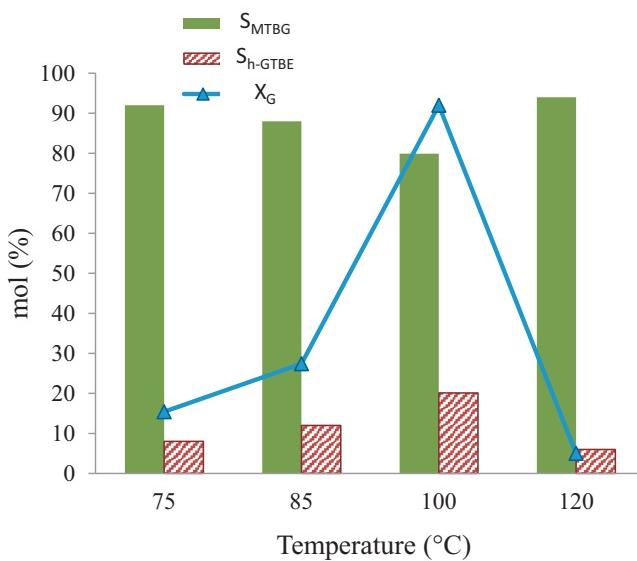


Fig. 8. Effect of reaction temperature on etherification of glycerol over C(10)AlPO(1.5)-250 under conventional heating. Reaction conditions: 5.0 wt.% of catalyst referred to the starting amount of glycerol, TBA/G molar ratio = 4 and 24 h of reaction time.

similar acidity values. Likewise, a comparison at isoconversion (values between 17 and 21%) indicates that the selectivity value to h-GTBE (13%) attained on MPTMS(10)AlPO(1)-50 was similar to those obtained on C(2.5)AlPO(1.5)-310 and C(4)AlPO(1.5)-310, although the STY value was practically half. These differences in activity among the catalysts obtained from different organosilica compounds could be ascribed to the lower acid strength of propyl-SO₃H sites in comparison to that of arene-SO₃H moieties, as it is well-known, in clear accordance with results previously reported by Melero et al. [11].

Based on present results, the role of the textural properties on catalytic behavior seems to be less relevant than that of the acidity, given that the porosity of all the catalysts (mesopores higher than 10 nm) was adequate to allow the diffusion of the reactant and product molecules through the pores, so there was no hindrance in the accessibility of the reactants to the catalytic sites. In fact, all the C(10)AlPO(y)-250 catalysts allowed us to detect TTBG, although in low amounts. The water removal could promote the formation of h-GTBE and in particular, of TTBG. Thus, several strategies for eliminating the water in the reaction medium have been reported [16,19,38], employing zeolites which increased the yield to DTBGs [16,19], or a water permselective membrane that increased the conversion and the yield to h-GTBE from 29% to 53% [38].

3.3.2. Etherification of glycerol by conventional heating

The effect of temperature on the catalytic activity under conventional heating is shown in Fig. 8 for C(10)AlPO(1.5)-250. It can be seen that up to 100 °C, the activity increase with temperature. However, a further increase of temperature to 120 °C led to a high decrease of the activity. This fact can be explained due to the high temperature together with the acidity of the solid, promoted a fast dehydration of TBA at the beginning of the reaction, increasing the formation of isobutylene from 3 wt.% (100 °C) to 6 wt.% (120 °C) and producing diisobutylene (3 wt.%). Thus, the formation of the desired products became difficult, according to [8,40] and to what we previously observed on a sulfonated hybrid silica [24].

Fig. 9 shows the variation of conversion and selectivity to different products with time of reaction on C(10)AlPO(1.5)-250. As can be seen, conversion increases with reaction time but the equilibrium is not reached even at 17 h. After this time, the conversion

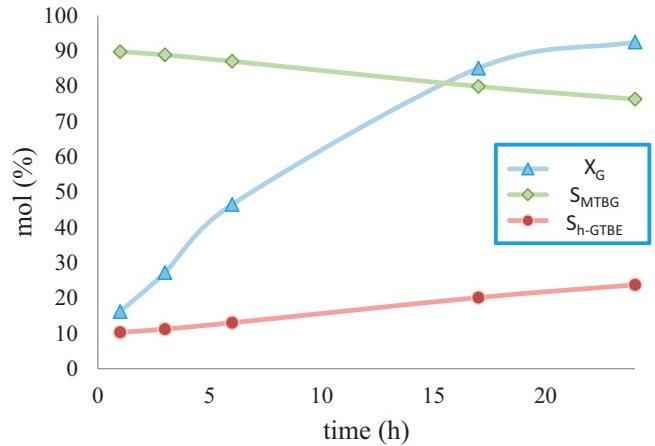


Fig. 9. Study of the variation of conversion and selectivity to the different products with time of reaction on C(10)AlPO(1.5)-250 at 100 °C and conventional heating. Experimental conditions as in Fig. 8.

hardly increases, indicating that equilibrium is almost reached. Based on these results, some of the synthesized catalysts were tested at 100 °C and 24 h. As was expected, the catalytic activity (Table 4) follows an analogous order than using Mw, being the C(10)AlPO(1.5)-250 again the most active catalyst ($Y_{h\text{-}GTBE} = 22\%$), indicating that acidity is the most important factor regardless of the way of heating. However, with the exception of this catalyst, the rest of them showed lower conversion and selectivity values than using microwaves. A possible explanation to these results is that the higher energy generated by the microwave, in comparison to the conventional heating, would give rise the breaking of the hydrogen bonds formed between the free hydroxyl groups (Al-OH; P-OH and Si-OH) and the sulfonic acid sites, even at lower temperatures. Similar results were found with a series of propylsulfonic and octyl co-functionalized propylsulfonic MCM-41 attaining better results with the co-functionalized solids due to the octyl groups partially palliate the interaction of the sulfonic groups with the silanol groups of the silica [41].

3.3.3. Comparison of the best catalyst here studied with other reported catalysts

The catalytic performance of the catalyst, with which the best results were obtained, was compared with the activity of some of the reported catalysts for the etherification of glycerol with *tert*-butyl alcohol, Table 5. First of all, the comparison was made for conventional heating, which is the way of heating employed by all the authors in literature. It can be seen that, under similar experimental conditions, i.e. a similar weight of catalyst and a similar TBA/G molar ratio, the yield to h-GTBE (22%) attained on C(10)AlPO(1.5)-250 at 24 h of reaction time was similar or slightly superior to some of the catalysts reported in literature, which employed lower reaction times but generally higher reaction temperatures [20–23]. However, the yield to h-GTBE (22%) was inferior to that obtained on a fluorinated beta zeolite (27%) at the same reaction time [19]. In addition, very recently, Srinivas et al. [17] reported the highest value of $Y_{h\text{-}GTBE}$ (40%) to date, over a cesium exchange tungstophosphoric acid supported on tin oxide, although the amount of catalyst employed was 27 wt.% in relation to the initial amount of glycerol, which was practically six times higher than the weight employed in the present study. Considering the STY value, where the active sites exhibited by the catalysts and the time employed are taken into account, it must be said that the value obtained on C(10)AlPO(1.5)-250 (1.7 h⁻¹) was also comparable to those obtained in literature, Table 5, with the exception of

Table 4

Catalytic behavior of the different catalysts after 24 h of reaction time under conventional heating. Reaction conditions: 5.0 wt.% of catalyst referred to initial glycerol, TBA/G ratio = 4, reaction temperature 100 °C.

Catalyst	Conversion (%)	S _{MTBG} (mol%)	Y _{h-GTBE} (mol%)	Site Time Yield (STY) (h ⁻¹)
C(2.5)AlPO(1.5)-310	9	89	1	0.3
C(4)AlPO(1.5)-310	12	89	1	0.2
C(10)AlPO(1.5)-250	92	76	22 (1) ^a	1.7
C(10)AlPO(1)-250	21	84	3 (1)	0.4
MPTMS(10)AlPO(1)-50	10	89	1	0.1

^a In parenthesis, yield to glycerol triether (%).

Table 5

Values of yield to h-GTBE (Y_{h-GTBE}) and STY (mmol of produced h-GTBE per mmol of active specie per hour) values obtained on the solids investigated here and on several catalysts reported in the literature.

Catalyst	time (h)	Weight of catalyst (wt.%)	Temperature (°C)	Y _{h-GTBE} (%)	STY (h ⁻¹)	References
20C ₁ TS	1	27	100	40	81.7	[17]
MFI-UL-100	12	5	120	20	8.7	[18]
FHB	24	5	75	27	5.4	[19]
AS-100	5	5	90	19	2.3	[20]
BCC-S5h	5	5	120	20	2.8	[21]
TC-L	10	5	120	20	0.6	[22]
BC 10:1-S2 h	8	5	120	20	1.7	[23]
C(10)AlPO(1)-250	24	5	100	22	1.7	This work
Starbon® acid ^a	15 min	54	100–120	Traces	Traces	[42]
C(10)AlPO(1)-250 ^a	15 min	5	85	21	152.0	This work
C(10)AlPO(1)-250 ^a	1	5	85	23	41.4	This work

^a Experiments carried out using Microwaves.

the value attained on the cesium exchange tungstophosphoric acid supported on tin oxide.

Despite the fact that the results under conventional heating obtained here are not the best to date, the good results obtained on Mw at short reaction times (15 min) are very remarkable, making this option very interesting for future research. In fact, the STY value obtained on C(10)AlPO(1.5)-250 under Mw is, to the best of our knowledge, the highest reported to date, partly due to the lack of data reported under this method of heating. In this sense, in the only experiment carried out under Mw [42], h-GTBE were not obtained.

3.3.4. Reusability and catalyst stability

The reusability of the solids was studied by consecutive etherification reactions. The C(4)AlPO(1.5)-250 and C(10)AlPO(1)-310 catalysts was evaluated after one run whereas the most active catalyst, C(10)AlPO(1.5)-250, was evaluated in four consecutive runs. As can be seen in Table 6, the yield to different products drastically dropped for the reused C(4)AlPO(1.5)-250 whereas the reused C(10)AlPO(1)-310 and C(10)AlPO(1.5)-250 exhibited a lower decrease of its activity. This different behavior could be related with the textural properties of the solids. The highest surface area and lowest pore size exhibited by C(4)AlPO(1.5)-250, would promote a high pore blockage and, as a consequence, a decrease in the activity of the reused solid, in clear agreement with data previously reported [19,24]. In fact, as can be seen in Table 6, the C(4)AlPO(1.5)-250 catalyst suffered the greatest decrease in its surface area.

For its part, the C(10)AlPO(1.5)-250 catalyst exhibited a similar catalytic activity, i.e., similar yield to the different products after the four cycles evaluated, although a slight decrease in the products yield was obtained, mainly after the first and second cycle, Fig. 10. As the acidity of the catalyst after the four runs, obtained from the amount of sulfur obtained by elemental analysis, was the same (1.1 mmol S/g) than that of the fresh one, Table 1, the leaching of the sulfonic groups should be ruled out. However, the adsorption of some substrates on the acid sites, mainly unreacted glycerol and some reaction products, would explain the small decrease in the activity observed after the two first runs, in clear accordance

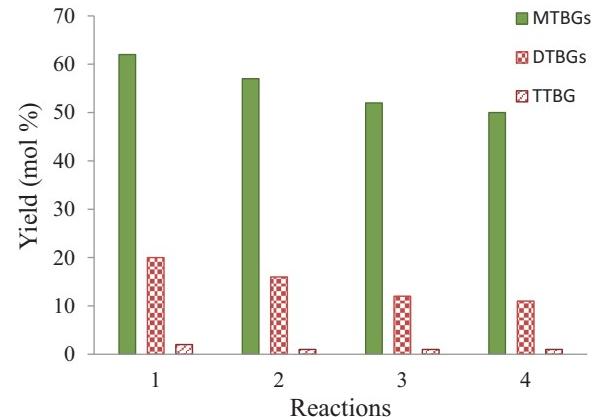


Fig. 10. Influence of the catalyst recycling on the catalytic activity in glycerol etherification reactions on C(10)AlPO(1.5)-250 at 85 °C. Experimental conditions as in Fig. 7.

with different authors [23,24]. However, it is important to mention that no activation treatment was performed on the catalysts after the reaction. To check this fact, a TGA of the reused solids shown in Table 6 was carried out. The profile obtained for the reused C(10)AlPO(1.5)-250 showed a weight loss of ~4% superior in respect to the fresh one in the range of 220–300 °C (Fig. S6). This weight loss could be assigned to glycerol molecules or some reaction products that remained strongly adsorbed on the solid after reaction, according to our previously results [24].

4. Conclusions

Organosilica-aluminum phosphates, (X)-AlPO(y)-T, were synthesized by a sol-gel method, using two different silica precursors 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (C) or 3-mercaptopropyltrimethoxysilane (MPTMS), with varying Al/P molar ratios ($y = 0.5\text{--}1.5$) and calcination temperatures ($T = 250$ and 310°C). All the solids exhibited amorphous character and porosity, mainly mesoporosity, although the macroporosity increased as the

Table 6

Yields to ethers and BET surface area values of several solids before and after 15 min of reaction, under MW irradiation.

^aAfter reaction.

^cAfter 4 runs.

Catalyst	Y _{MTBGs} (%)	Y _{DTBGs} (%)	Y _{TTBG} (%)	S _{BET} (m ² /g)
C(4)AlPO(1.5)-250	15 ^a	2 ^b	2 ^a	210 ^a
C(10)AlPO(1)-310	34	20	7	42 ^a
C(10)AlPO(1.5)-250	62	50 ^c	21	79

^aBefore reaction.

^bAfter reaction.

^cAfter 4 runs.

aluminum content decreased. As the aluminum content decreased, materials with less surface area and higher macroporous character, were obtained. In addition, an interaction between Al and Si, as well as Al and P, was evidenced by MAS NMR. Furthermore, a decrease in the Al-P interaction was observed, as the Al/P ratio diminished. The materials exhibited acidities ranging from 0.3 to 1.2 mmol SO₃H/g, obtained from TGA. The highest value of acidity was attained in the synthesized materials with the greatest amounts of organosilica and aluminum.

These solids were tested on the microwave-assisted etherification of glycerol with *tert*-butyl alcohol at 85 °C and at autogenous pressure. The catalytic activity of the solids was directly related to its acidity. In addition, oxidized MPTMS(10)AlPO(1) materials, with similar acidity and textural properties to C(10)-AlPO materials, exhibited less activity due to the lower acid strength of the propyl-SO₃H groups, in comparison with the arene-sulfonic ones. The C(10)AlPO(y)-250 catalysts exhibited a higher capability to produce h-GTBE than the Amberlyst-15. Furthermore, the highest yield to h-GTBE (21%), equivalent to a STY value of 152 mmol h-GTBE/mmol SO₃H h⁻¹, was attained on the most active catalyst, C(10)AlPO(1.5)-250 under Mw. This STY value is, to the best of our knowledge, the highest reported to date. However, in general, the activity attained under conventional heating was inferior to that obtained under microwave, even at higher temperatures and reaction times.

A decrease in the surface area and the pore volume values of the solids after reaction took place, associated with the blockage of the pores. Thus, a high percentage of macropores, as well as the large size of the mesopores, as exhibited by C(10)AlPO(1.5)-250, seem to be key factors in avoiding the loss of activity in subsequent runs.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.05.007>.

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